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Temperature-associated changes in groundwater quality

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ABSTRACT

Climate change and urbanization are currently leading to a warming of the subsurface worldwide with yet unforeseen consequences for groundwater quality. The temperature-sensitivity of chemical and biological processes suggests that small temperature changes driven by current warming should have a detectable effect on the ecology of aquifers and the composition of groundwater itself, but field observations covering temperatures that are environmentally relevant are sparse. The analysis of a large data set provides field-scale evidence that, within the naturally occurring temperature range between 5 and 20 °C, temperature affects the quality of groundwater. A difference in temperature of +1 K is linked to a 4% decline in oxygen saturation and a pH drop of 0.02 due to the accumulation of carbon dioxide. Further, warmer groundwater shows signs of enhanced mineral weathering and higher concentrations of drinking water-relevant elements such as manganese. The observed trends in groundwater quality are consistent with a temperature-associated intensification of microbial metabolic rates and enhanced organic matter mineralization at warmer temperatures either within the aquifers or in the overlying soils. A times series analysis reveals that soil and groundwater temperatures in the studied area have been increasing at a rate of 0.1–0.4 K per decade -comparable to recent global warming- driving subtle, but distinct changes in groundwater pH and oxygen concentrations. The results confirm, that certain but central aspects of groundwater quality (pH, O_2, pCO_2, Mn, DOC) change due to warming, which may increase the costs for purification when drinking water is produced from groundwater resources and may turn some aquifers uninhabitable for groundwater biota.

1. Introduction

Roughly half of the world's population relies on groundwater for potable water supply and more than 40% of globally used irrigation water is subtracted from groundwater (Siebert et al., 2010; WWAP 2009). The use of groundwater as a resource for different proposes critically depends on the amount and quality of the available groundwater. While quantitative projections of the future availability of groundwater have been developed (Famiglietti, 2014; Rodell et al., 2018; Taylor et al., 2013), projections of future groundwater quality are far from being realized. Many factors affect groundwater quality such as land use and land use change, aquifer lithology or soil type which have been subject to past studies (e.g., Appelo and Postma, 2005; Böhlke, 2002; Chapelle, 2005; Hansen et al., 2018; Scanlon et al., 2005), but the effect of warming on the chemical composition of groundwater remains poorly quantified (Bates et al., 2008; Green et al., 2011; Klove et al., 2014; Lipczynska-Kochany, 2018a; Sophocleous, 2004; Taniguchi et al., 2007). This is surprising because temperature regulates key biological and chemical processes that affect the cycling of oxygen, carbon and other elements in soil and groundwater. Examples of such temperature-dependent processes are microbial respiration and growth rates, mineral solubility's and diffusion rates of solutes in water (Addy et al., 2016; Appelo and Postma, 2005; Jørgensen et al., 2009; Lloyd and Taylor, 1994; Price and Sowers, 2004).

Most of the presently available knowledge on temperature-associated changes in groundwater quality is derived from studies on geothermal energy use (subsurface heat storage). Using primarily laboratory batch and column experiments in the temperature range between 0 and 100 °C these studies concluded that temperature-related changes in groundwater composition are only significant for temperatures > 40 °C, except for As, which was already mobilized at moderate temperature increases (Bonte et al., 2013; Brons et al., 1991; Griebler et al., 2016). However, a recent in-situ subsurface heating experiment showed that even small temperature changes below 25 °C may already have an impact on groundwater quality. Although the study was hampered by strong groundwater level fluctuations, it found that a warming of the aquifer by only 7 K leads to observable changes in the concentration of elements and substances such as Mg, Si, Li, and ammonium (Saito et al., 2016).

More evidence for a temperature-control on aquifer biogeochemistry comes from studies on the fate of organic matter and organic pollutants. Enhanced desorption of organic compounds such as natural

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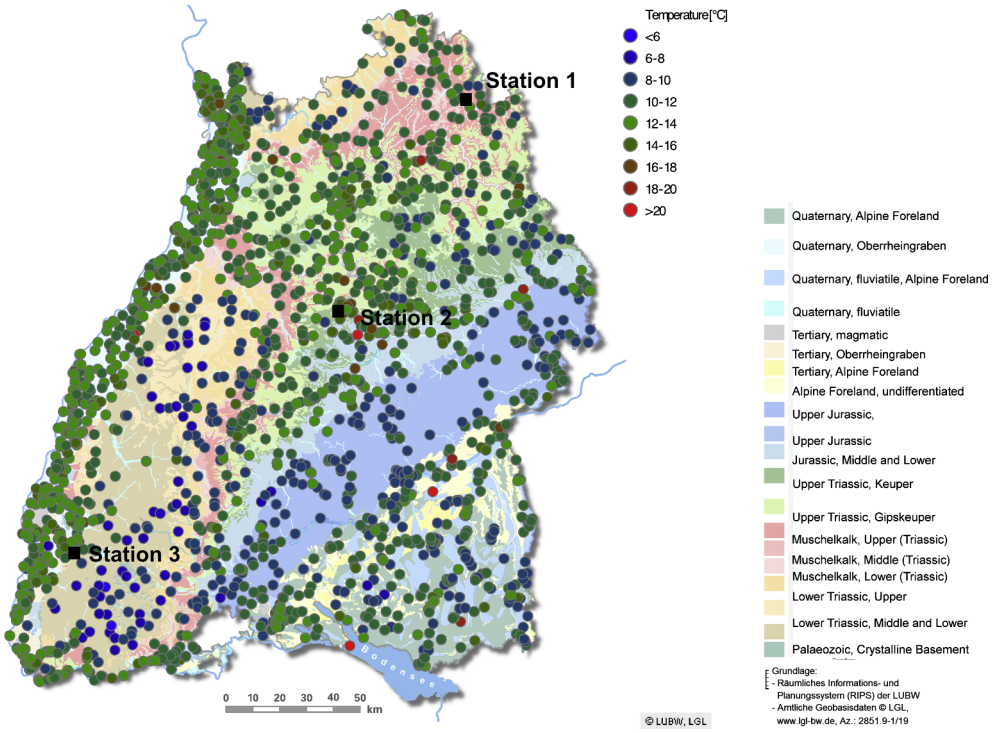

Fig. 1. Map of the study area and location of the sampling points. A color code indicates the average groundwater temperature observed at each sampling point. Major regional geological units are illustrated. A brief description of the geological units is given in Supplementary Table S1. Locations with available time series of soil temperature data are indicated as black dots (Stations 1–3).

organic matter or organic contaminants from soils and sediments has been observed as a result of increasing temperatures (Brons et al., 1991; Kaiser et al., 2001; Wang et al., 2010). A warming-induced increase in the solubility of pollutants either directly or by increasing the solubility of natural organic matter, which in turn enhances the solubility of pollutants via complexation, may therefore also be expected (Bloomfield et al., 2006; Sposito and Weber, 1986). The temperature-induced mobilization of humic substances may further add to higher rates of pollutant degradation by stimulating microbial activity (Lipczynska-Kochany, 2018b).

Higher temperatures may also directly accelerate degradation of organic pollutants in groundwater. For example, an increase in reductive dechlorination after an increase of in-situ temperatures from 10 to 25 °C has been reported by Ni et al. (2015). Further, thermodynamic data suggests that concentrations of inorganic pollutants such as heavy metals should decrease with warming (with the exception of those occurring as anions such as Arsenic) providing some evidence that temperature increases may be beneficial for water quality (Bonte et al., 2014).

Temperature changes may also have an impact on the redox chemistry of groundwater. For example, in a set of column experiments warming from 10 to 70 °C resulted in a shift of the observed redox conditions as the biogeochemical conditions changed from oxic respiration to iron and sulfate reduction (Jesußek et al., 2013). There is also evidence, that groundwater redox chemistry may be sensitive to natural temperature fluctuations of only a few degrees. In a study on 65 groundwater samples from Chihuahua, Mexico, a moderately significant negative correlation between temperature and oxidation-reduction potential has been observed (Prieto-Amparan et al., 2018). Studies on the influence of seasonally varying temperatures of surface waters recharging aquifers during bank filtration in France and Germany found a positive correlation between temperature and Mn concentrations as well as a negative correlation between temperature and oxygen concentrations (Bourg and Bertin, 2002; Massmann et al., 2008).

Other evidence from laboratory studies suggests that biological processes are easily affected by temperature changes. Warming of only a few degrees may already lead to a change in the microbial community structure and groundwater fauna (Brielmann et al., 2009).

However, global warming will not only lead to temperature changes within aquifers (Anderson, 2005; Taniguchi et al., 2007), it may also alter biogeochemical cycles in soils overlying the aquifers. Because recharge connects soil water with groundwater, temperature-induced changes in soil water chemistry should become detectable in the composition of groundwater in the long run. Although the exact response of the soil microbial community to warming is a matter of discussion there is ample evidence that warming may stimulate microbial respiration (Davidson and Janssens, 2006). It can be expected, that the current increase in soil heterotrophic respiration (Bond-Lamberty et al., 2018) will inevitably change the cycling of soil carbon and other elements in soils, for example, by increasing dissolved organic carbon production (Lipczynska-Kochany, 2018a). However, other consequences of climate change such as changes in soil moisture and atmospheric CO_2 may strongly modulate the microbial response to warming (Castro et al., 2010). Especially, soil moisture impacts microbial activity, and the anticipated changes in global hydrological cycles (Huntington, 2006) may therefore modify the response of soil microbial communities to warming to some extend (Mandal and Neenu, 2012).

Overall, the findings of earlier studies call for a more widespread investigation of the link between subsurface temperatures and groundwater quality, especially in the lower temperature range (< 20 °C). Groundwater temperature changes associated with climate change are not expected to be as severe as under the conditions of a commonly applied aquifer thermal energy storage. Therefore, the aim of this study was to quantify temperature-associated changes in groundwater using field observations that are relevant for the temperature range naturally occurring (i.e. without heat manipulations). In particular, focus will be given to the influence of temperature change on biochemically mediated reactions that largely control subsurface oxygen and carbon cycling.

2. Methods

2.1. Study site

The study area (Federal state of Baden Württemberg) is located in

southwestern Germany and encompasses an area of 35,752 km^2. Land use is dominated by agricultural land (~46%), followed by forest (~36%); the remaining area consists of urban land use including space for transit (roads, railways and associated land) (LUBW, 2014).

The average air temperature is 9.5 °C. Precipitation is around 70 mm per month in winter and 110 mm in summer. The timing of groundwater recharge varies. Generally recharge is highest in winter and spring, when soils are saturated.

The geological setting of the study area shows a large variety of hydrogeological units (Fig. 1, Supplementary Table S1). Groundwater samples were taken from wells and springs located in a diverse range of geological units. Major hydrogeological units comprise fractured Paleozoic rocks (magmatic and metamorphic), a mesozoic series of carbonate rocks and porous sedimentary rocks, and unconsolidated cenozoic sediments. Groundwater chemistry shows a large variety as a result of the different hydrogeological settings i.) Groundwater in Paleozoic aquifers, that mostly consist of igneous (predominantly granitic) and metamorphic rocks, is slightly acidic and shows low mineralization, ii.) Groundwater in mesozoic, and quaternary aquifers is mildly mineralized and mostly of the Ca-HCO_3-type. Evaporitic Triassic rocks host waters of the Ca-SO_4 type as well as Na-Cl-rich waters.

The average groundwater temperature measured in the sampling period from 2000 to 2015 was 10.6 °C with 90% of all observations lying in the range between 6.7 and 14.9 °C (Supplement Fig. S3). The western part of the study area is subject to elevated geothermal gradients in the upper few kilometers of the continental crust, which did not show any effect on the here observed temperature distributions within the upper 40 m. No apparent differences between shallow and deeper groundwater exists in the data set used, except that deeper groundwater (depth-to-groundwater table > 30 m) appears to be somewhat colder as compared to shallower groundwater (Supplementary Fig. S5). Notably, groundwaters sampled from fractured rocks in the regions with predominately mesozoic rocks usually exhibit somewhat lower temperatures, probably because of a shorter residence time as compared to sandy, quaternary aquifers.

2.2. Data analysis

To quantify the effects of temperature and of temperature changes on groundwater quality, data from a comprehensive groundwater monitoring was used. Groundwater data was retrieved on 10.01.2017 from the federal database of the Landesanstalt für Umwelt, Messungen und Naturschutz, Baden-Württemberg (LUBW), Germany (http://jdkgw.lubw.baden-wuerttemberg.de/servlet/is/200/). The data set is publicly available and has previously been used to investigate multiple pathways of Uranium mobilization and immobilization in groundwater (Riedel and Kübeck, 2018).

The monitoring network consists of a total of 2,021 sampling sites resulting in an observational density of ~1 location per 20 km^{-2} (Fig. 1). Most sampling locations are monitoring wells or wells used for groundwater abstraction to produce drinking water. About 530 locations are springs, which have been excluded from the original analysis and were analyzed separately. Two types of springs emerge in the study area, which can be separated using electric conductivity (Supplementary Fig. S4). Springs with electric conductivities equal to or higher than 30 mS m^{-1} were defined as “high mineralization” springs. Accordingly, springs with less than 30 mS m^{-1} were defined as “low mineralization” springs. In this respect, the terms “high” and “low” were chosen arbitrarily, simply to distinguish between the two populations.

The data is part of a continuous groundwater quality monitoring and covers samples taken between January 2000 and December 2015. Most locations were sampled two to six times per year. However, only samples taken during summer sampling campaigns (July/August) were used in this study, because they provide the most continuous record of groundwater temperature and quality. Samples from other periods of the year were taken less frequently as compared to the summer sampling campaigns and have therefore not been considered for the present analysis in order to avoid a potential bias in the data due to seasonality and sampling frequency. For all samples oxygen, pH, conductivity and temperature data is available. The parameters were immediately determined in the field during continuous pumping. In addition, for each sampling location (well or spring) at least one full scale analysis of the major ion chemistry was available (in addition to the temperature, pH and oxygen data) allowing to investigate the relation between temperature and water quality in unprecedented detail. All parameters were analyzed using ISO (International Organization for Standardization) standardized methods. The calculation of dissolved pCO_2 is derived from measurements of pH, temperature and alkalinity (Appelo and Postma, 2005). Samples outside the temperature range from 5 to 20 °C were not considered, because the low abundance would have not enabled a statistically sound analysis (Supplementary Fig. S3).

In a first step the data set was used to establish a relation between groundwater temperature and composition based on data that is available for 1486 wells. If more than one analysis was available for a given sampling location results were averaged to remove a potential bias towards the more frequently analyzed locations. A linear regression model was then fitted to the data using Matlabs (© Mathworks, 2013) polyfit function. A test for the level of significance for each regression was performed using the corrcoef function. Significant results were defined for *P*-values of less than 0.001 (Johnson, 2013).

In a second step, a time series analysis was conducted using sampling locations with a continuous record of T, oxygen concentrations and pH values from 2000 to 2015. For the time-dependent analysis a data set including all observations was constructed. Again, only data from the summer sampling campaigns was considered in order to remove a bias towards seasonality. To facilitate comparison between the different sampling sites all of the T, pH and oxygen-saturation data of each time series were normalized to the respective average of a time series. A linear regression model was then fitted to the time series data. The resulting trends are expressed as change in value of parameter per year.

Some samples exhibited concentrations of dissolved manganese, fluoride, dissolved organic carbon (DOC), oxygen or potassium, which were below the limit of quantification (LOQ). All values below the reported limit of quantification were censored to the reported LOQ to create a consistent data set. This did not affect the presentation and interpretation of the data, because the LOQ was always below the 5th quantile of all samples, i.e. no more than 5% of the samples had concentrations of a certain parameter below the LOQ. However, by doing so, gradients calculated on basis of the regression analysis were slightly lower as compared to other ways of data censoring such as replacing data below the LOQ with values of zero or with values of half the LOQ. The estimated trends are therefore more conservative, as gradients might be steeper than the ones reported here. The list of LOQs is shown in Supplementary Table S2.

Daily soil temperatures from three locations within the study area hosted by the Deutsche Wetterdienst (Offenbach, Germany) were available for the years from 1970 to 2017 (Station 1: Bad Mergentheim, Station 2: Stuttgart, Station 3: Freiburg). The location of the respective stations is indicted in Fig. 1. The soil temperature was measured in 5 cm depth. Yearly values were obtained by averaging the daily observations for each year.

3. Results and discussion

Within the temperature range between 5 °C and 20 °C consistent trends in groundwater chemistry are observed. Groundwater sampled in wells was associated with lower pH values and lower oxygen saturations at higher temperatures as compared to groundwater with lower temperatures (Fig. 2). Ordinary least square regression analysis shows that a temperature difference of +1 K is, on average,

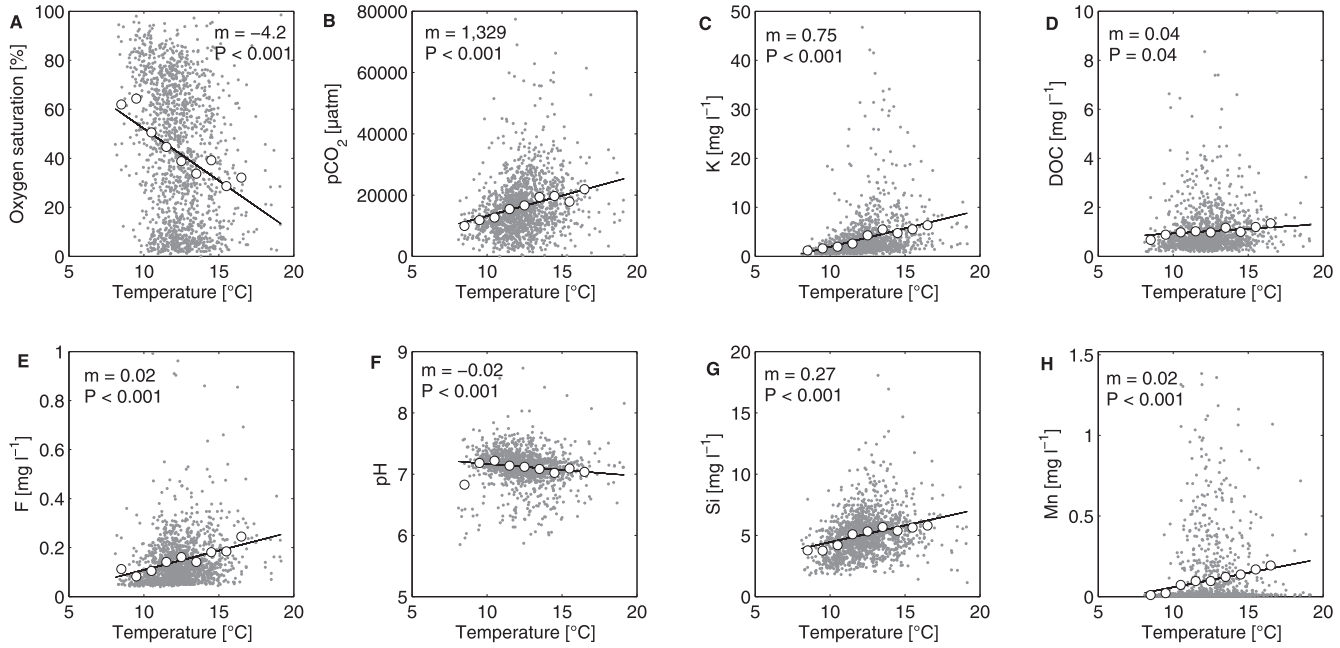

Fig. 2. Temperature differences are associated with differences in groundwater quality. Relation between *in-situ* groundwater temperature and saturation of dissolved oxygen (A), pCO_2 (B), potassium (C), dissolved organic carbon (D), fluoride (E), pH (F), Si (G) and Manganese (H) in groundwater sampled in n = 1486 wells. m denotes the trend for a given parameter associated with a temperature change of +1 K calculated using an ordinary least regression analysis. *P* indicates the statistical level of significance for the regression analysis. In addition, parameter values were binned at increments of 1 K. The averages calculated for each bin are indicated by the white circles.

accompanied by a difference of −4% for oxygen saturation, and a pH drop by 0.02 units (Fig. 2). Dissolved organic carbon (DOC), potassium, fluoride, manganese, silicium and pCO_2 show the opposite trend, i.e. values commonly increase at higher temperatures (Fig. 2).

Groundwater sampled at springs generally exhibited cooler temperatures with an average of 9 °C (for comparison, groundwater sampled in wells shows an average temperature of 12.5 °C), which is close to the average yearly air temperature of 9.5 °C in the study area. Springs with high mineralization showed similar temperature-associated changes in groundwater composition as compared to wells (Supplementary Fig. S1). Also, springs with low mineralization showed similar results to wells with the exception of pCO_2 and pH (Supplementary Fig. S2). This has been expected, because springs with low mineralization often occur in terrains with fractured rocks (Springer and Stevens, 2009), where contact time with aquifer material is short and groundwater often is in contact with the atmosphere allowing rapid outgassing of CO_2.

This time-independent analysis can be validated by the predictions made from the findings. Rising temperatures increase concentrations of DOC and potassium at a rate of 0.04 and 0.75 mg l^{-1} K^{-1}, respectively. This is comparable to those concentration changes observed during a recent subsurface heating and cooling experiment (Saito et al., 2016).

The time-dependent analysis reveals a similar picture. Groundwater sampled at wells and springs showed significant increases in temperature in the study area (Table 1). The rate of temperature change is comparable to the rate of global warming during the past decades of 0.02 K yr^{-1} (Xu et al., 2018). While temperature increased, oxygen saturations and pH values decreased (Table 1). Albeit the relatively short period of time (16 years), the analysis shows that changes in groundwater chemistry due to warming are detectable in the present data set and follow patterns comparable to those observed in the time-independent analysis (Fig. 2). Interestingly, the observed temperature increases are comparable in magnitude to the increases observed in the upper soil at three different sites within the study area (Fig. 3). This suggests that warming of the shallow subsurface is responsible for the observed temperature trends in groundwater.

Notably, T increases are higher in groundwater sampled at springs as compared to groundwater sampled in wells (Table 1). Especially, the temperature increase of 0.03 K yr^{-1} observed in springs is almost similar to the temperature changes of 0.03–0.04 K yr^{-1} observed in the upper soil horizons in the study area (Fig. 3). This was an expected finding, because springs often respond rather quickly to environmental changes, because of the relatively short residence times of groundwater discharging at springs (Jyväsjärvi et al., 2015; Springer and Stevens, 2009).

The observed temperature-dependent trends in groundwater composition likely result from a number of different processes. First, microbial respiration is temperature-dependent (Lloyd and Taylor, 1994; Price and Sowers, 2004). Absolute respiration rates are not available for the study site. But temperature-dependent changes in relative

Table 1
Changes in temperatures, pH and oxygen concentrations observed in 530 springs and 1468 wells during the period from 2000 to 2015. m denotes the change of each parameter per year obtained by a regression model. * indicates a statistically significant trend at a level of significance of $P <= 0.001$. ns = not significant ($P > 0.001$).

	No. of sampling locations	No. of samples	Temperature trend [K yr^{-1}]	Oxygen saturation trend [% yr^{-1}]	pH trend [yr^{-1}]
Wells	1,468	21,122	0.012*	−0.24*	−0.003*
Springs (high min.)	129	2,033	0.026*	−0.17*	−0.004*
Springs (low min.)	401	6,017	0.030*	−0.15*	(0.008)ns

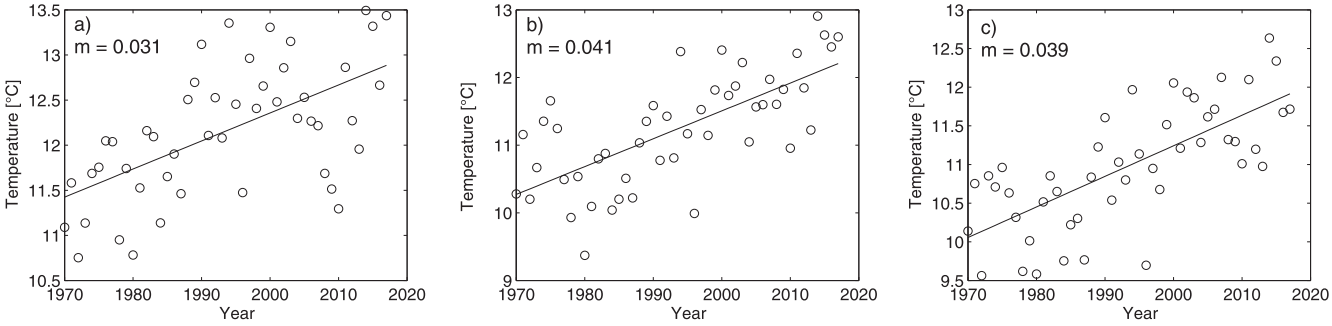

Fig. 3. Times series of the yearly averaged soil temperatures measured at 5 cm depth at three different observational points in the study area (Data: Deutscher Wetterdienst). (a) Station 1, (b) Station 2, (c) Station 3. The location of each station is indicated in Fig. 1. The straight lines illustrate the results obtained by a linear regression model with m denoting the change of soil temperature per year in K yr^{-1}. All trends are highly significant ($P < 0.001$).

respiration rates generally show uniform trends across ecosystems and climates in soil and groundwater, i.e. respiration rates commonly increase by a factor of approximately 3 to 4 when temperature increases from 5 to 20 °C (Addy et al., 2016; Lloyd and Taylor, 1994; Jørgensen et al., 2009). Higher respiration rates are well reflected by lower oxygen saturations as well as the greater accumulation of CO_2 in warmer groundwater as compared to colder groundwater (Fig. 2). Second, as oxygen concentrations decrease an increase of DOC concentrations is observed. The relation between DOC and T in wells is only moderately significant ($P < 0.05$), but is well supported the findings of previous research. Sorption of dissolved organic matter to soil material is temperature sensitive. At higher temperatures a thermally induced mobilization of DOC from the mineral matrix occurs, which increases its availability as a microbial substrate (Brons et al., 1991; Kaiser et al., 2001). As a result oxygen is increasingly depleted via microbial respiration, whereas concentrations of manganese subsequently increase, owing to a shift towards more reducing conditions. A similar shift towards more reducing conditions as indicated by lower oxidation-reduction potentials has been found in groundwater from an agricultural area in Mexico (Prieto-Amparan et al., 2018). The DOC released appears to be more aromatic at higher temperatures, because the specific ultraviolet absorbance, SUVA, (measured as the absorbance at 254 nm normalized to the DOC concentration) also increases with 0.06 l mg^{-1} m^{-1} K^{-1} in wells ($P < 0.001$; data not shown). One possible explanation is that the solubility of aromatic organic carbon increases with temperature. Another is, that microbial respiration preferentially mineralizes non-aromatic organic carbon leaving behind a more refractory aromatic carbon.

Warmer groundwater was also associated with higher Si, K and F concentrations, the latter being a groundwater contaminant of concern in several regions of the world. These observations are attributed to an intensification of mineral dissolution. For example, feldspar dissolution, which releases Si and K, is a function of temperature with higher dissolution rates occurring at higher temperatures (Welch and Ullman, 2000). Dissolution rates at 20 °C determined under abiotic conditions in the laboratory are two to three times higher than at 5 °C (Welch and Ullman, 2000). Warmer temperatures should thus lead to an enhanced release of K and Si to groundwater from mineral dissolution. The total concentration of K and Si in solution will then only be limited by the subsequent formation of secondary minerals. In addition, the observed increase of pCO_2 in groundwater with increasing T suggests that more carbonic acid is present in warmer groundwater, which is likely to further enhance mineral weathering (Hansen et al., 2018).

It is worth noting that the here observed trends are the result of biogeochemical processes in the soil-groundwater continuum (most groundwater recharge occurs after water has percolated through a soil) (Kindler et al., 2011). Because shallow groundwater temperatures (< 30 m) are mostly a function of the land surface temperature (Benz et al., 2017) it is possible that some of the here observed trends point to temperature-dependent biogeochemical processes that occurred prior to recharge in the soils overlying the respective aquifers. This would mainly have consequences for the flux of gaseous components to groundwater. For example, soil warming results in an enhanced release of CO_2, some of which is dissolved in soil solution to form carbonic acid, which either reacts with minerals or eventually recharges to groundwater (Kindler et al., 2011). Warmer recharge temperatures have indeed been found to correlate with groundwater pCO_2 (Jurgens et al., 2010). However, not all of the CO_2 released in soils by microbial respiration gets dissolved, instead it rather directly emits to the atmosphere. Thus, the exchange of soil air with the atmosphere limits the flux of CO_2 to groundwater.

Another factor to consider when interpreting the results is irrigation. Recharge occurs primarily during the winter month in the study area. When recharge is artificially increased in the warmer growing season due to enhanced irrigation in agricultural areas, the composition and temperature of the soil water recharging to groundwater will change. During the summer month more CO_2 is present in soils due to the combined effects of microbial and root respiration. As a result, irrigation of agriculturally used land in summer leads to the recharge of warmer water with more CO_2 dissolved in it (Hansen et al., 2018; Jurgens et al., 2010). In these cases, the relation between temperature and groundwater quality is the result of an increase in the proportion of recharge during the warmer summer month. However, irrigation is more pronounced in arid regions. In the here studied area, irrigation is currently not expected to play a major role, although irrigation demand may increase in the future.

In summary, because processes in soil cannot unambiguously be separated from those in groundwater with the currently available data, the present study essentially identifies the cumulative effects of both.

One constraint of this study is, that it is limited to a small region in central Europe. It remains to be seen, if aquifers in other hydroclimatic settings respond similarly to temperature changes. However, the observed relation between certain groundwater quality parameters and temperature is statistically robust and in line with other studies from Mexico and Japan (Prieto-Amparan et al., 2018; Saito et al., 2016). Therefore, the results add to the growing body of evidence that small temperature changes likely have a detectable effect on groundwater quality. But the scatter in the data is large (Fig. 2), because numerous other factors also influence the chemical composition of groundwater such as land use, soil type and local geology. For example, urbanization influences groundwater quality not only by warming the subsurface (“urban heat island”), but also via other aspects such as pollution with nutrients, salts or organic contaminants (Bruce and McMahon, 1996; Hansen et al., 2018; Hobbie et al., 2017; Scanlon et al., 2005). Agriculturally used land receives large amounts of nutrients including K, which eventually accumulates in soil and groundwater (Böhlke, 2002; Scanlon et al., 2005). Aquifer lithology is also important, because the presence or absence of minerals as well as their solubilities dictates the

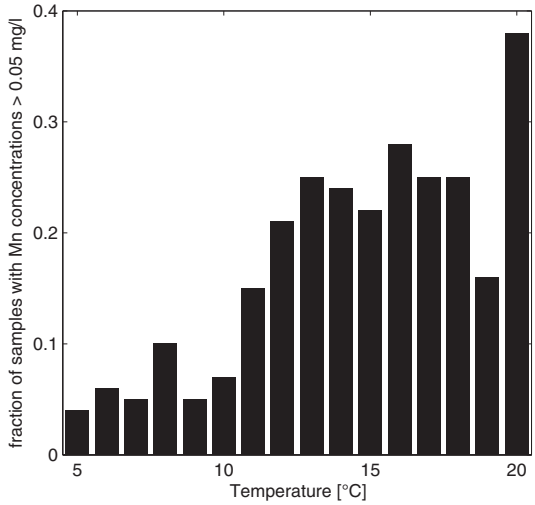

Fig. 4. Fraction of samples that exhibit Mn concentrations above the German drinking water guideline of 0.05 mg l^{-1}. Samples were binned in steps of 1 K.

ion composition of groundwater (Appelo and Postma, 2005; Chapelle, 2005). Differences in mineral abundances in the diverse geological settings of the studied area (Fig. 1) likely explain the scatter of the Si, K and F data. Finally water-table depth has a large influence on the redox chemistry of groundwater. Shallow water-table depths are often associated with higher DOC and Mn concentrations and lower oxygen concentrations as compared to deeper water tables (Pabich et al., 2001; McMahon et al., 2019).

It should further be noted, that, besides the here discussed increases in groundwater temperatures, numerous other consequences of climate change and urbanization are expected that may also influence groundwater quality (Green et al., 2011; Taylor et al., 2013). For example, climate change-induced changes in the hydrological cycle will lead to shifting recharge patterns (Taylor et al., 2013). A shift of the timing of recharge in regions where soil microbial activity and vegetation show a pronounced seasonality may have an impact on the chemical composition of groundwater as well. Changes in soil moisture availability itself may also have an impact soil microbial community structure and activity (Castro et al., 2010). Droughts, sea level rise and perhaps changes in vegetation may differently affect soil water and groundwater quality. Currently, there are many different aspects of climate change (besides warming) whose effects on groundwater quality are difficult to predict. Hence there is a need for more studies dealing with the impact of hydroclimatic changes on soil water and groundwater quality.

4. Conclusions

The analysis of a large data set provides evidence for a biogeochemical link between subsurface temperature and groundwater quality. Several implications arise from this observation with respect to a potential warming of soil and groundwater. First, groundwater biota, i.e., stygobiotic organisms, are sensitive to ambient conditions in groundwater and only thrive at high oxygen levels (Dole-Olivier et al., 2009; Maurice and Bloomfield, 2012). Because oxygen is crucial for groundwater fauna a decrease in oxygen concentrations due to warming will turn some aquifers uninhabitable for these organisms. Second, when groundwater is used as a resource for drinking water production, in some cases quality deteriorations will make additional efforts for purification necessary (Lipczynska-Kochany, 2018a). For example, increases in DOC and Mn will necessarily require higher dosages of flocculants to reduce the risk of microbial contamination, to prevent the deposition of manganese oxides in drinking water distribution systems and to keep Mn concentrations below guideline values. This is further illustrated in Fig. 4. The fraction of samples with Mn concentrations above the guideline value for drinking water in Germany steadily increases from less than 10% to more than 30% in the temperature range between 5 and 20 °C. Also, formation of disinfection byproducts will increase at elevated DOC concentrations when chlorine is used for disinfection. Further, acidification due to elevated pCO_2 requires degassing/neutralization in order to ensure that the produced drinking water is non-corrosive. Third, increases in weathering rates increase the salinity of groundwater, which may enhance the problem of soil salinization in arid regions, where irrigation demand is high (Hansen et al., 2018).

Groundwater temperatures are expected to rise locally as well as globally as a result of urbanization and global warming (Bates et al., 2008; Beltrami et al., 2006; Huang et al., 2000; Menberg et al., 2013; Taniguchi et al., 2007). Modelling results indicate that increases of 3–4 K in shallow groundwater are possible within the next decades (Taylor and Stefan, 2009). Additionally, local temperature gradients of 3–7 K are observed underneath larger cities (Menberg et al., 2013). However, the influence of warming on subsurface biogeochemical cycles and on groundwater quality is currently not considered in projections of future freshwater availability (Bates et al., 2008; Famiglietti, 2014; Rodell et al., 2018; Taylor et al., 2013). Clearly, as quality issues will further amplify the already existing problem of groundwater depletion due to climate change, good groundwater governance needs to include a thorough management of groundwater temperatures to secure groundwater quality and quantity in the future.

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Author information

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Data availability

The data used for this study is available from Landesanstalt für Umwelt, Messungen und Naturschutz, Baden-Württemberg (LUBW) ["http://jdkgw.lubw.baden-wuerttemberg.de/servlet/is/200/"] or upon request from the author.

Conflict of interest

None declared.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2019.02.059.

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